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PERFORMANCE OF THE UNION CARBIDE DISSOLVED OXYGEN ANALYZER

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by

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Research Laboratory

Program Element 1HA327

NATIONAL ENVIRONMENTAL RESEARCH CENTER
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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report is part of a continued effort by the Instrumentation Development Branch, Methods Development and Quality Assurance Research Laboratory, NERC, Cincinnati, to evaluate instruments and provide information to both users and suppliers. It is also intended that instrumentation be upgraded and that a choice of the most suitable instrument can be made for a particular application.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

PERFORMANCE OF THE UNION CARBIDE DISSOLVED OXYGEN ANALYZER

The Union Carbide Dissolved Oxygen Analyzer, Model 1101, was evaluated to determine the effectiveness of the thallium electrode in the measurement of dissolved oxygen. This report summarizes the results of performance tests which included, stability, transient response, linearity, and temperature compensation. Data obtained indicated long-term instability due to dissolved oxygen (DO) sensor drift, instrument calibration dependence upon dissolved solids content of the sample, instrument ground loop problems, and excessive transient response to changes in sample temperature.

INSTRUMENT DESCRIPTION

The Union Carbide Dissolved Oxygen Analyzer consists of a sensor assembly and a signal conditioning unit located in an electronics cabinet. The dimensions are as follows:

1.	Electronics Cabinet	21cm x 29cm x 10cm deep
2.	Sensor Assembly	25cm long x 9.8cm diameter

The general specifications for this instrument as is listed in the Union Carbide Operating Instructions are as follows:

1.	Power:	115 V, 60 Hz, 1/10 ampere
2.	Range:	0.1 - 15 ppm D.O.
3.	Accuracy:	± 0.2 ppm over full range ± 0.5°C
4.	Response Time:	95% of full scale in 15 seconds
5.	Recorder Output:	0-50 mv
6.	Operating Temperature:	0-50°C (compensated)
7.	Ambient Temperature Effect:	Temperature compensated within 1% from -1°C to 37°C

8. Maximum Recommended Distance Between Probe and Electronics Cabinet: 152 meters.

The sensor assembly contains a thallium electrode formed in a ring about a reference electrode. A temperature sensitive resistor (Sensistor) is housed within the cylinder. The thallium ring and reference electrode is a galvanic cell with the half-cell potential of the thallium being responsive to D.O. content in solution. The Sensistor is said to perform the dual function of temperature compensation and temperature measurement.

The signal conditioning unit consists of a solid state (FET) operational amplifier complete with power supply, calibration potentiometers, and an output linearizing module. The linearizing module converts a negative logarithm output to a linear output proportional to D.O. in solution. This linear output is connected to a meter calibrated for D.O. in ppm and temperature in degrees centigrade. The meter is backed by a mirror to reduce reading errors due to parallax. A 0-50 mv recorder can be connected to a terminal strip mounted within the electronic cabinet.

THEORY

The operating principle of this measurement is: D.O. in solution will react with thallium in the reversible reaction forming thallium hydroxide.

$$4\ Tl + O_2 + 2\ H_2O \rightleftharpoons 4\ Tl\ (OH) \qquad (1)$$

The thallium hydroxide, in turn, will dissociate

$$4\ Tl\ (OH) \rightleftharpoons 4\ Tl^{+} + 4\ (OH)^{-} \qquad (2)$$

The result is that a half-cell potential is produced by the thallium in contact with its ions (Tl^{+}). The half-cell potential will vary as the D.O. in solution varies. The half-cell potential produced by the thallium and that of the reference electrode is Nernstian and can be described by the equation:

$$E = E_o - \frac{0.592}{n} \log Tl^+_a \quad (@25°C)$$

where E_o is the standard potential of the cell, Tl^+_a is the activity of the thallium ion, and n is the valence. The potential produced forms the input to the signal conditioning unit.

PERFORMANCE

The first objective was to determine the long term stability of the D.O. sensor. To accomplish this objective the following apparatus were utilized:

1. a temperature controlled water bath (Forma Scientific) equipped with an internal pump to provide continuous sample flow across the sensor
2. a recorder (Esterline-Angus) with variable span capability of 0 to 100 mv
3. titration apparatus and the necessary chemicals to perform Winkler determinations
4. a compressed air source diffused to produce saturated D.O. in solution.

The temperature of the water bath (tap water) was controlled at 25°C. Repeated observations were made of the D.O. sensor's performance after calibration. In each case, an upward drift resulted in the recorded output of the essentially constant dissolved oxygen in the sample. Figures 1, 2, and 3 illustrate three of these tests. Figure 2 illustrates the characteristic drift after substitution of a silver-silver chloride reference electrode in the circuit. (The measured potential of the Ag - Ag Cl reference electrode is within 10 mv of that used by Union Carbide.) The thallium electrode was filed smooth and immediately placed in the sample except for the results shown in Figure 2, which is merely a continuation of the calibration of Figure 1. Since similar results were obtained (drift) with the use of the Ag - Ag Cl and the two reference electrodes provided by Union Carbide,

the drift was obviously the result of the thallium electrode. Figure 3 indicates the recorded D.O. to be 7 ppm high after a 7-day interval. This drift was accelerated if the thallium was exposed to air for a period of time. Thus, the thallium is quite susceptible to oxidation in air.

A literature review* of the properties of thallium indicated that the chloride ion would possibly interfere with the reaction of equation (2). Thallium chloride does not dissolve easily and its formation interferes with the oxidation of thallium. Five-year averages with maximum and minimum values for pH, dissolved solids, and the chloride ion were obtained from the Cincinnati Water Works for finished water.

	5-year average	Maximum	Minimum
pH	8.6	8.1	8.9
Dissolved solids (Total), ppm	327	533	230
Chloride ion, ppm	47	87	23

A stability test was performed in distilled water to minimize any effect of dissolved solids. A very unstable output (noisy) was overcome by preconditioning the thallium surface in tap water through the usual initial transient interval. When steady state was attained, the sensor was returned to the distilled water sample and a stable output was obtained. The distilled water has a pH of 6, total dissolved solids of less than 2 ppm and chloride ion of less than 1 ppm. Figure 4 illustrates the results of this test.

The indicated, upward drift was very much less than that of the tap water tests. After 8-1/2 days of operation, the recorded indication was too high by 2 ppm. Although this test in distilled water neither proved nor disproved chloride ion interference, it did present a more stable medium in which the D.O. sensor could be observed in further performance tests.

*Encyclopedia of Science and Technology, Volume 13, McGraw Hill.

Distilled water samples were used in further testing to avoid excessive sensor drifts. Three sample baths were controlled at 5°C, 20°C, and 35°C. A D.O. calibration was performed in the 20°C bath after stable temperature and D.O. saturation had been attained.

The D.O. sensor was transferred from the 20°C sample to the 5°C sample to establish

1. the effectiveness of temperature compensation
2. the transient response to a temperature change.

As illustrated in Figure 5, an exceedingly long transient interval resulted before the steady state value was reached (15 hours). In addition, an erroneous D.O. indication in excess of 3 ppm resulted at the steady state value.

The D.O. sensor was returned to the 20°C sample, and the response is illustrated in Figure 6. The transient response was 40 minutes, and the D.O. indications returned approximately to that of the calibration value of the previous day.

The D.O. sensor was transferred from the 20°C sample to the 35°C sample, and the response is illustrated in Figure 7. A long term drift was experienced to reach a steady state value. Some of this may be the result of adding distilled water to replenish the evaporating sample. The final value was erroneous (too high by 2.5 ppm).

Finally the D.O. sensor was returned to the 20°C sample from the 35°C sample. The response is illustrated in Figure 8. A similar response, of shorter duration, to that of the 20°C to the 5°C exchange occurred. The total response was 7 hours. Vigorous wiping with tissues midway through this response had no effect in reducing the transient interval.

From the foregoing results, it was determined that temperature has a marked effect on the reaction rates of Equations (1) and (2).

Generally, the reaction rate is affected most by an exchange of the D.O. sensor from a higher to a lower temperature sample. Equilibrium, apparently, can be disturbed for hours by sudden changes in temperature. The cause of erroneous steady state indications from sample to sample was thought to be the result of a ground loop problem between the test apparatus and the D.O. analyzer. If this were true, inadequate temperature compensation could not be implied from the foregoing results.

To determine if a ground loop existed, the three water baths were used to control distilled water samples at 20°C. Two of these baths were allowed to saturate with D.O., and the third was purged of oxygen with nitrogen gas. Figure 9 illustrates the results of this test. It is readily apparent that the 4 ppm difference between water baths number one and number two is the result of ground loops. This sample is distilled water from the same still and controlled at the same temperature with Winkler determinations differing by only 0.05 ppm. The only difference, then, is that of the water baths and the indeterminacy of their respective ground loops with that of the signal conditioning unit. Note also that the 15 second response time listed in the Union Carbide specifications is met only when changing from a higher to a lower D.O. sample at the same temperature. When changing from a lower to a higher value, the response time is greater than 1 minute (Figure 9).

A test for linearity in the distilled water sample indicated that a recalibration was necessary. The complete procedure given in the operating instructions were followed in an attempt to calibrate the instrument. However, the span values were 8.8 ppm (679.15 mv) and 1.5 ppm (707.15 mv), which were determined in the distilled water sample. When the calibration was performed using these voltage inputs, the D.O. zero control could not be adjusted for proper agreement at 1.5 ppm. The minimum attainable panel meter reading was 2.0 ppm with the D.O. zero control at its lower mechanical stop. Calibration dependence upon sample characteristics was confirmed by successfully calibrating the instrument with a tap water sample.

The Union Carbide Dissolved Oxygen analyzer was installed and operated under field conditions at the test station on the Little Miami River. The tests were inconclusive because a portion of the thallium ring totally dissolved within the test interval. D.O. offsets and drift however, were observed during the 1 week of operation.

The temperature system was calibrated prior to the collection of the D.O. data. The panel meter versus an NBS calibrated thermometer were:

NBS thermometer	Panel meter
5.0°C	5.1°C
35.0°C	35.25°C

The response time in reaching steady state after transferring the sensor from a 35°C bath to a 5°C bath is illustrated in Figure 10. The time required to reach within 95% of the full scale value was in excess of 4 minutes. Figure 11 illustrates the exchange from 5°C to 35°C. Again, the time required to reach within 95% of the full scale value was in excess of 4 minutes.

DISCUSSION

In summary, there are problems associated with the Union Carbide D.O. sensor that would require correction. These problems are:

1. long-term instability because of sensor drift
2. calibration dependence upon dissolved solids content of the sample
3. ground loop between the sample medium and the signal conditioning unit
4. excessive response times of signals because of temperature changes.

The drift encountered in repeated tests of the sensor's performance in tap water samples would suggest an interference with the

reactions of Equations (1) and (2). A selective membrane approach would apparently be needed to overcome this problem.

The instrument calibration depended upon dissolved solids content of the sample. An interference is indicated to the reaction of thallium and oxygen in solution. Possibly, a stable, noninterfering electrolyte could be used with the conventional galvanic cell approach to the measurement of D.O. A membrane, an electrolyte, and a two-element electrode could be used. This, in turn, would overcome the ground loop problem of having the thallium in direct contact with the sample.

The excessive response time of signals because of temperature changes has been indicated by sequentially transferring the D.O. sensor through 5°C, 20°C, and 35°C baths. It has been determined from this that the chemical reaction rates are adversely affected. Correction for this may be insurmountable for the sensor in its present form. Again, if the conventional galvanic cell approach is pursued, the problem may be avoided.

The accuracy of the temperature system was adequate and within Union Carbide's specifications. The response time, however, was excessive. The response time can be improved if the Sensistor is moved from within the probe body to closer contact with the sample.

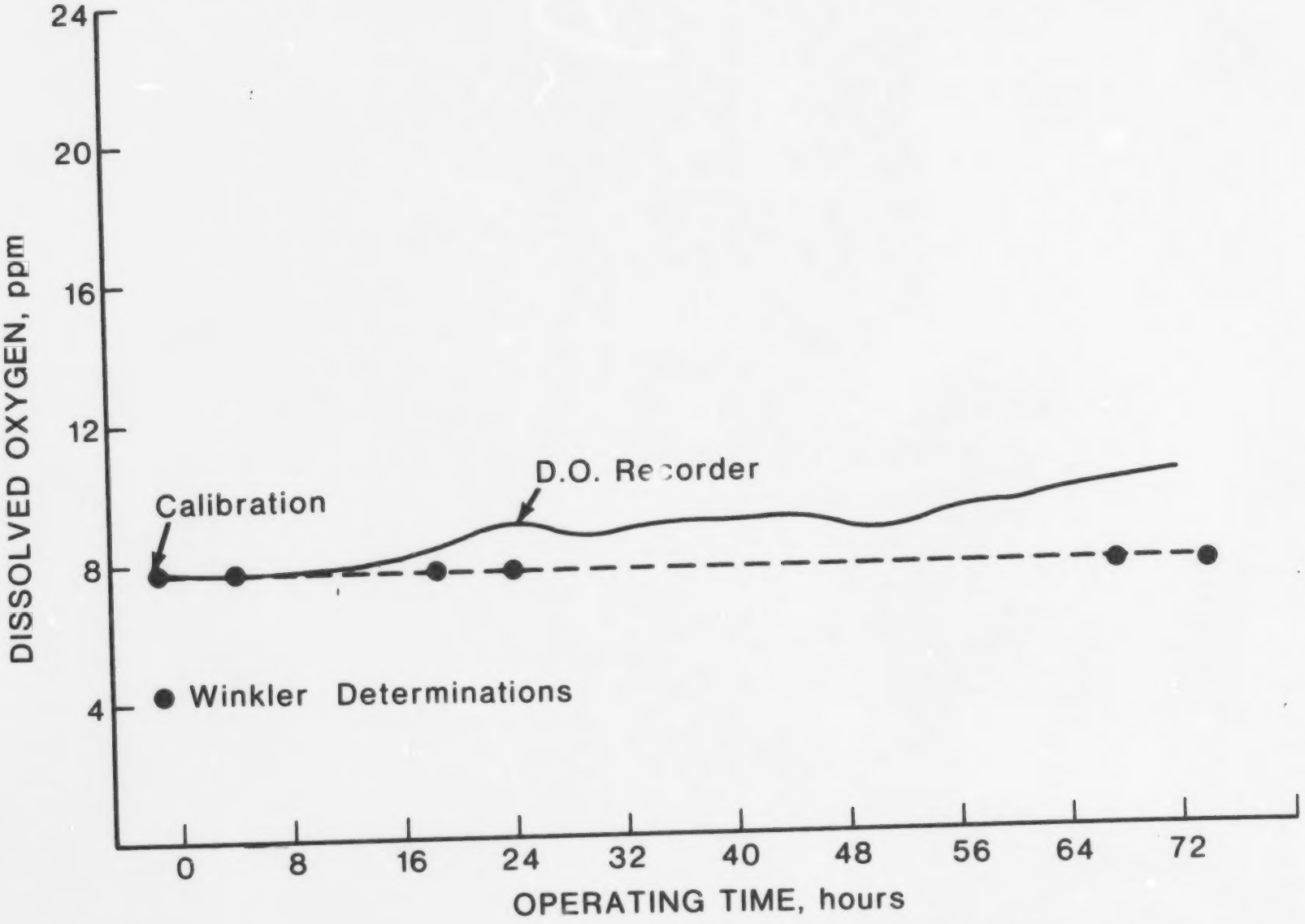

Figure 1. Sensor Drift after Calibration

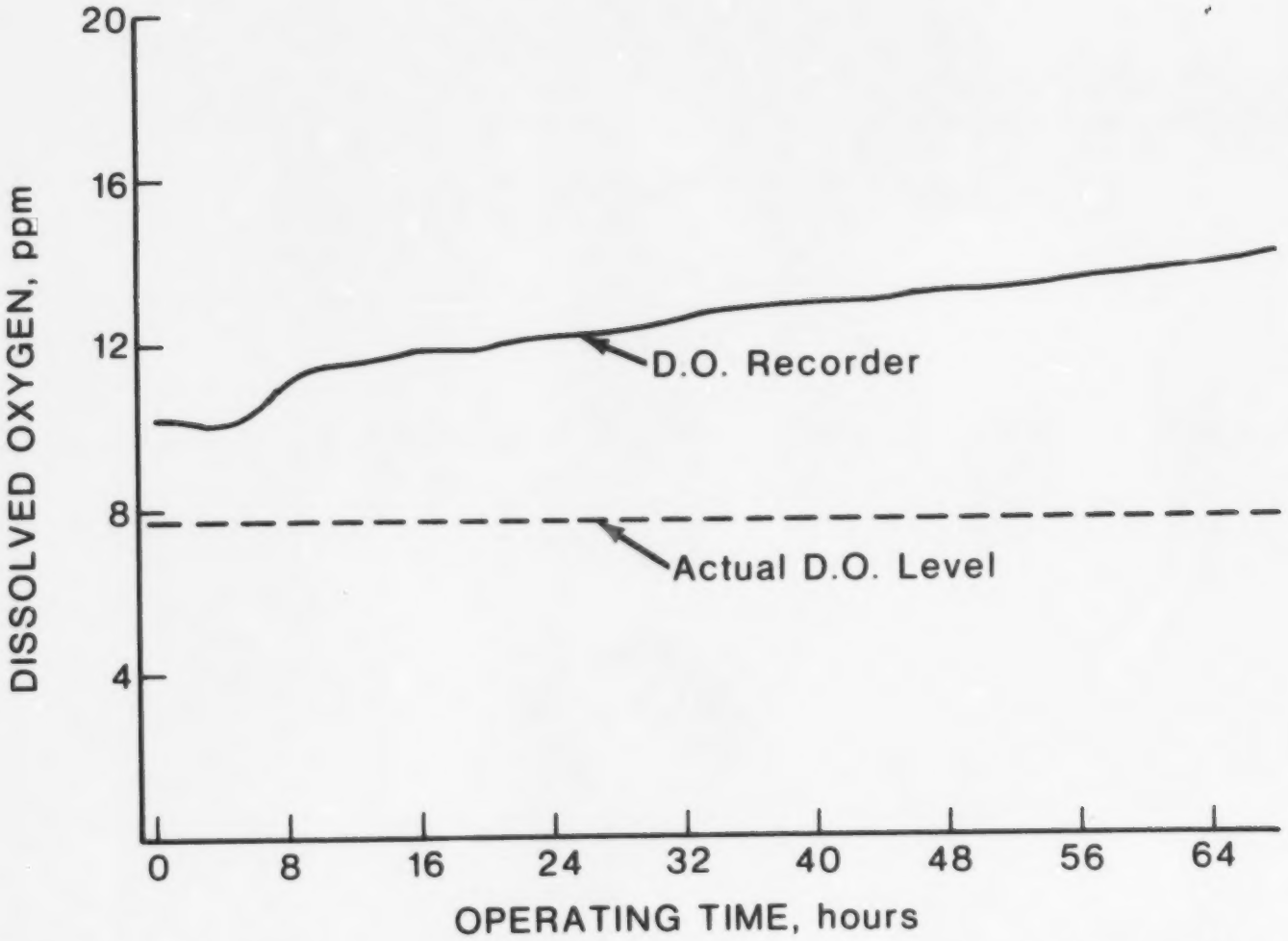

Figure 2. Sensor Drift after Insertion of Ag·AgCl Reference Electrode

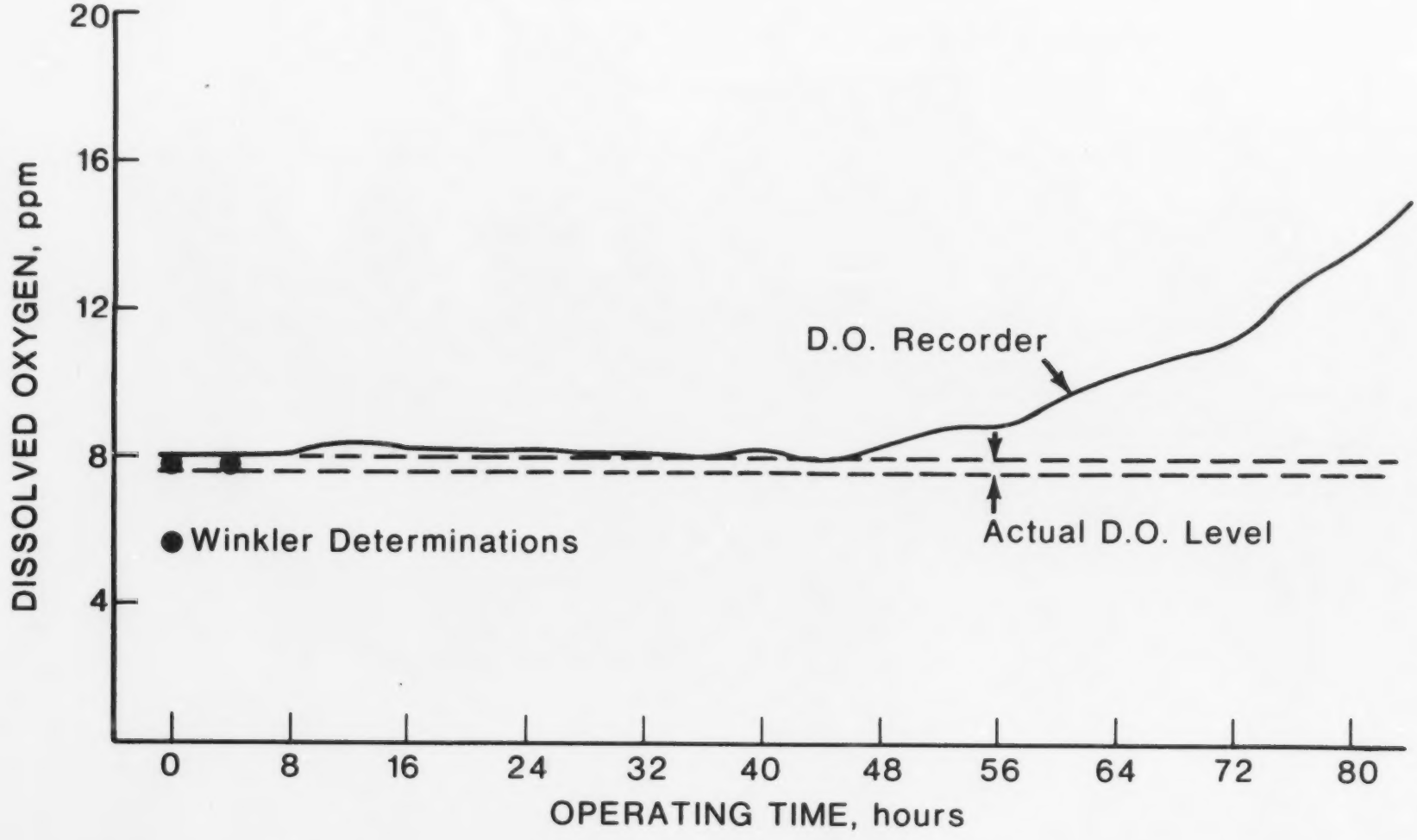

Figure 3. Sensor Drift after Filing Thallium Ring

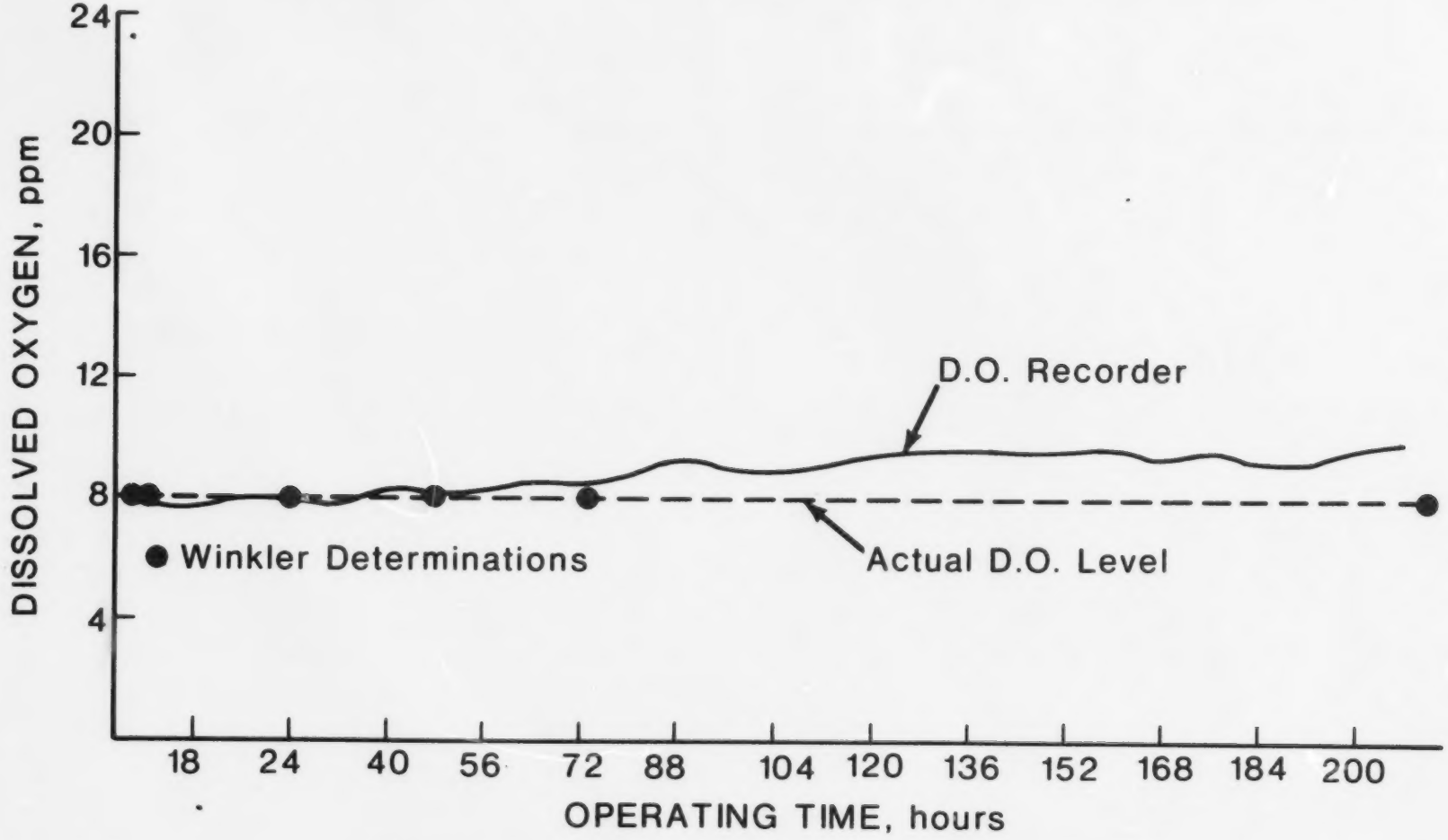

Figure 4. Sensor Drift in Distilled Water

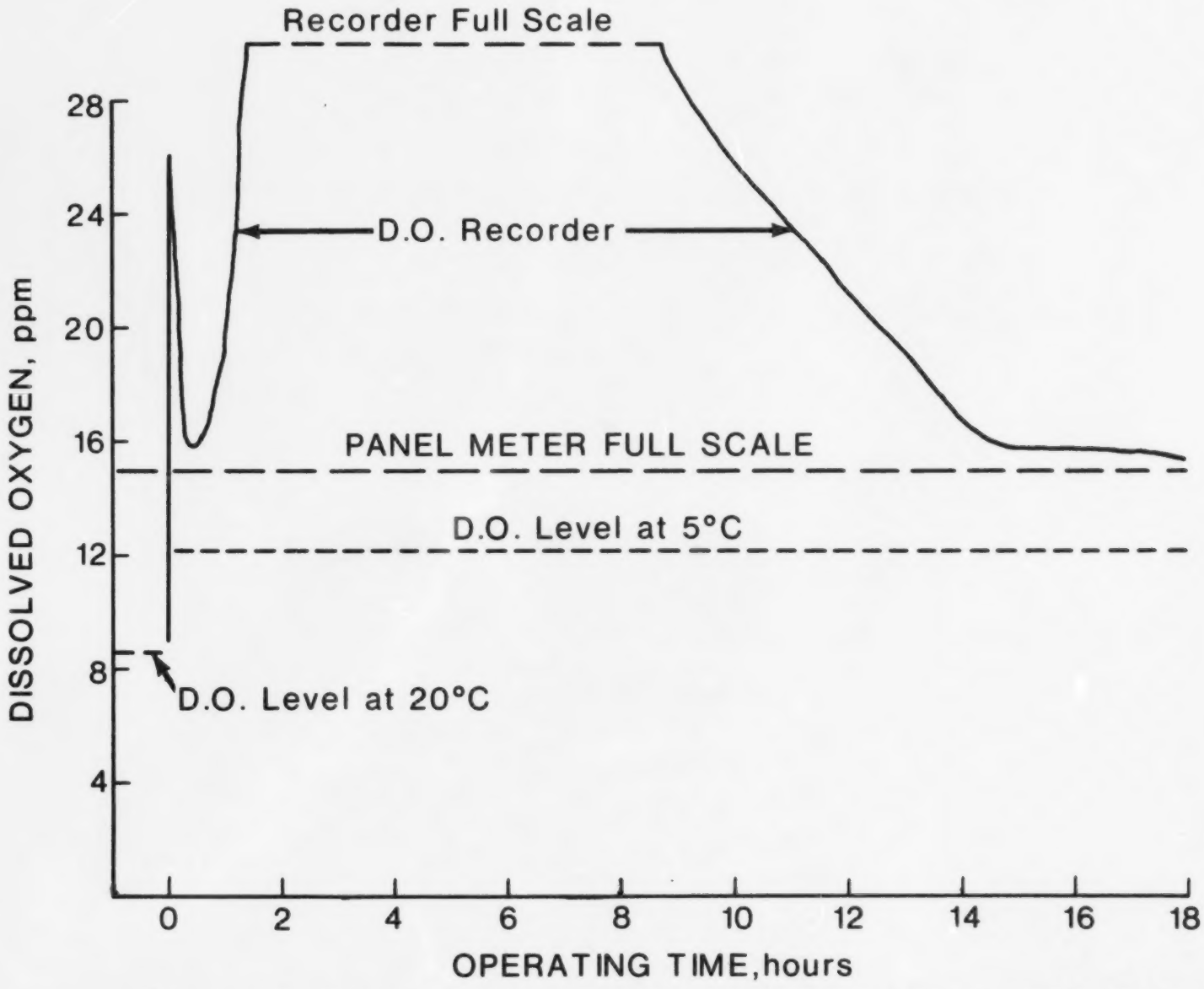

Figure 5. Sensor Transfer from 20°C Bath to 5°C Bath

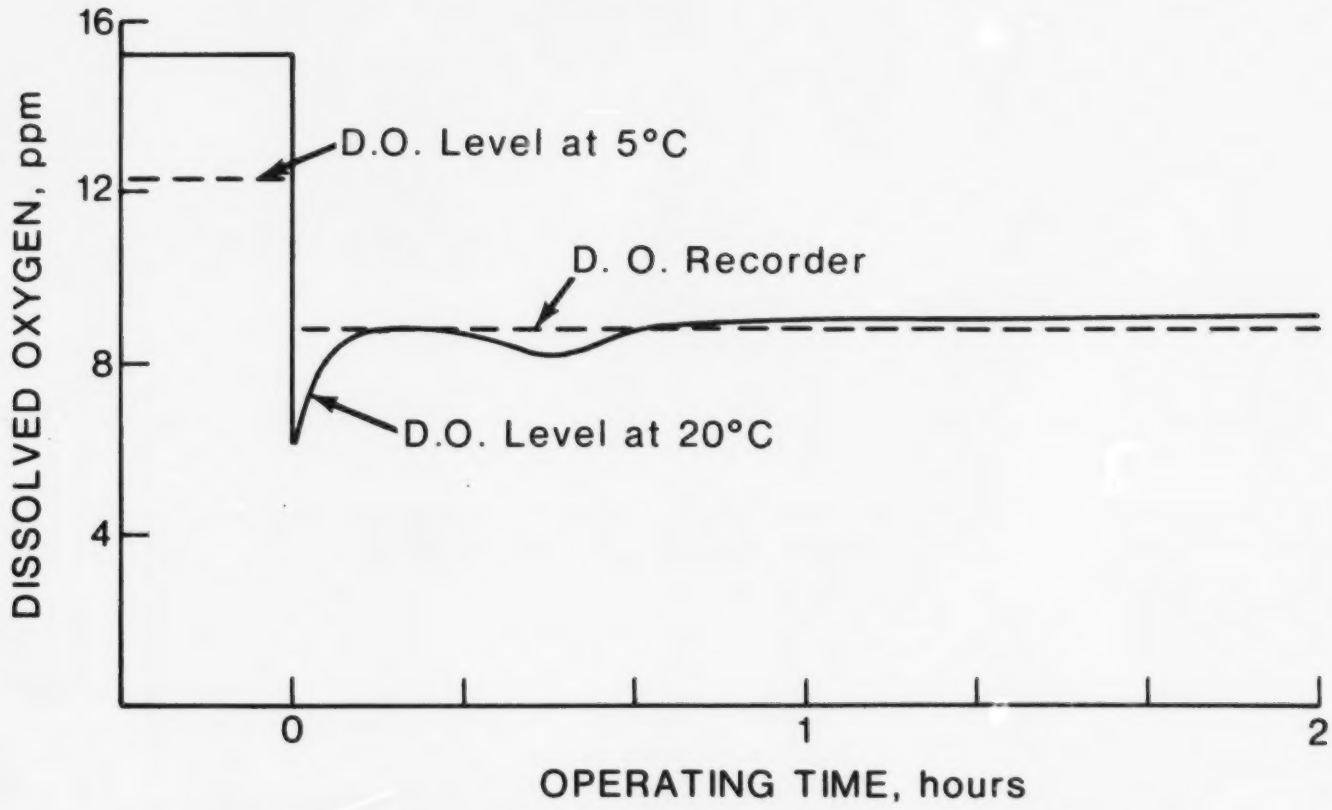

Figure 6. Sensor Transfer from 5°C Bath to 20°C Bath

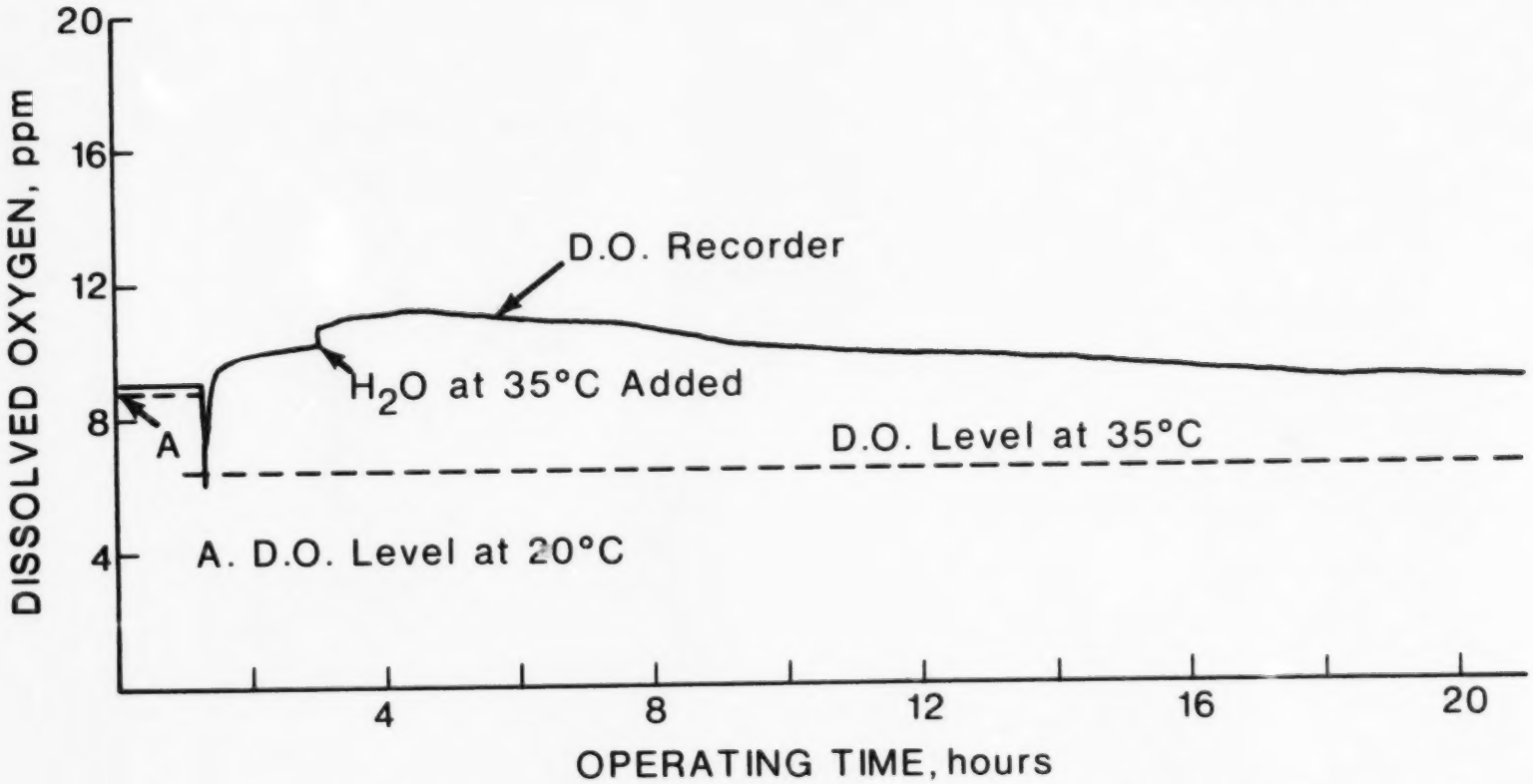

Figure 7. Sensor Transfer from 20°C Bath to 35°C Bath

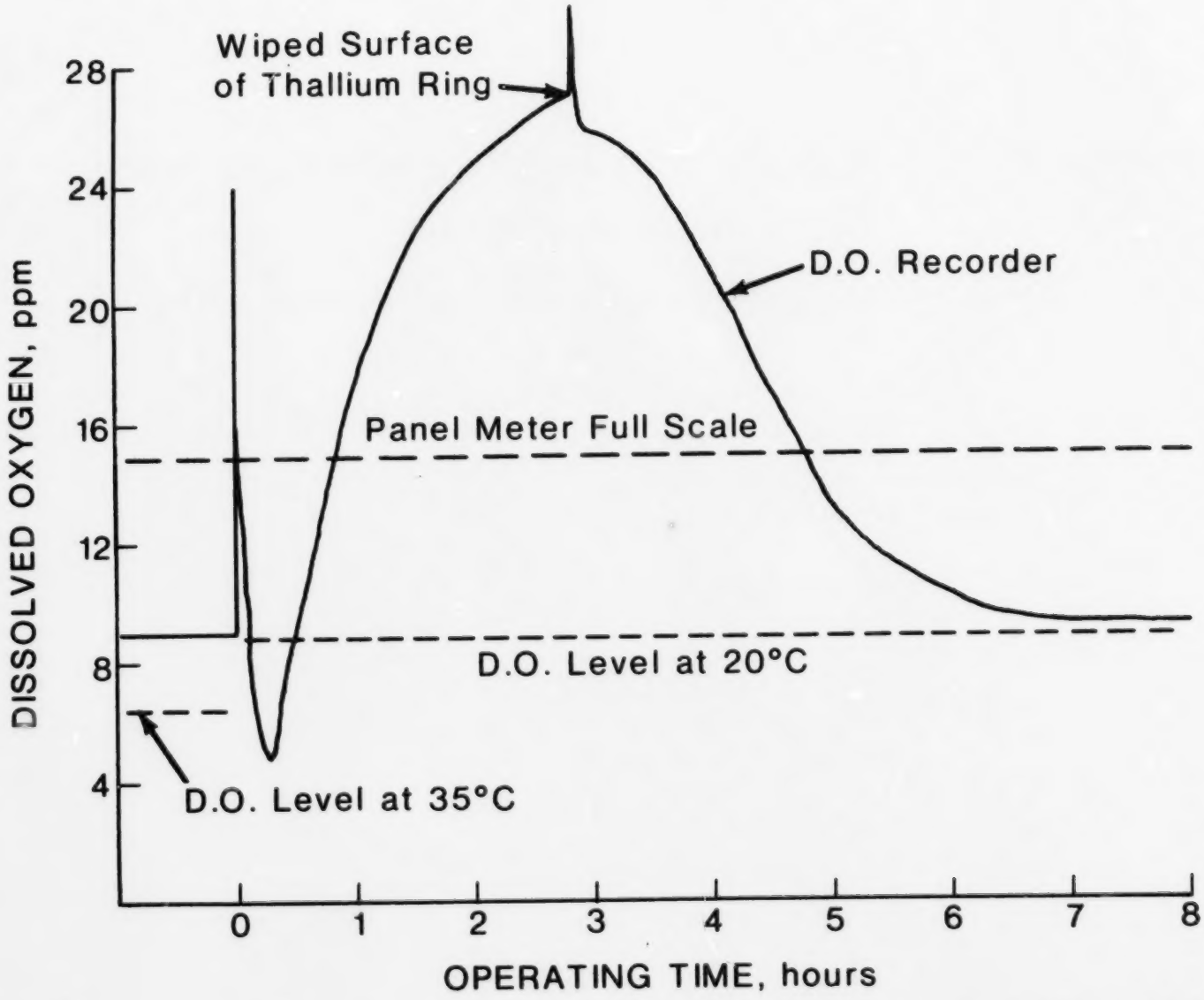

Figure 8. Sensor Transfer from 35°C Bath to 20°C Bath

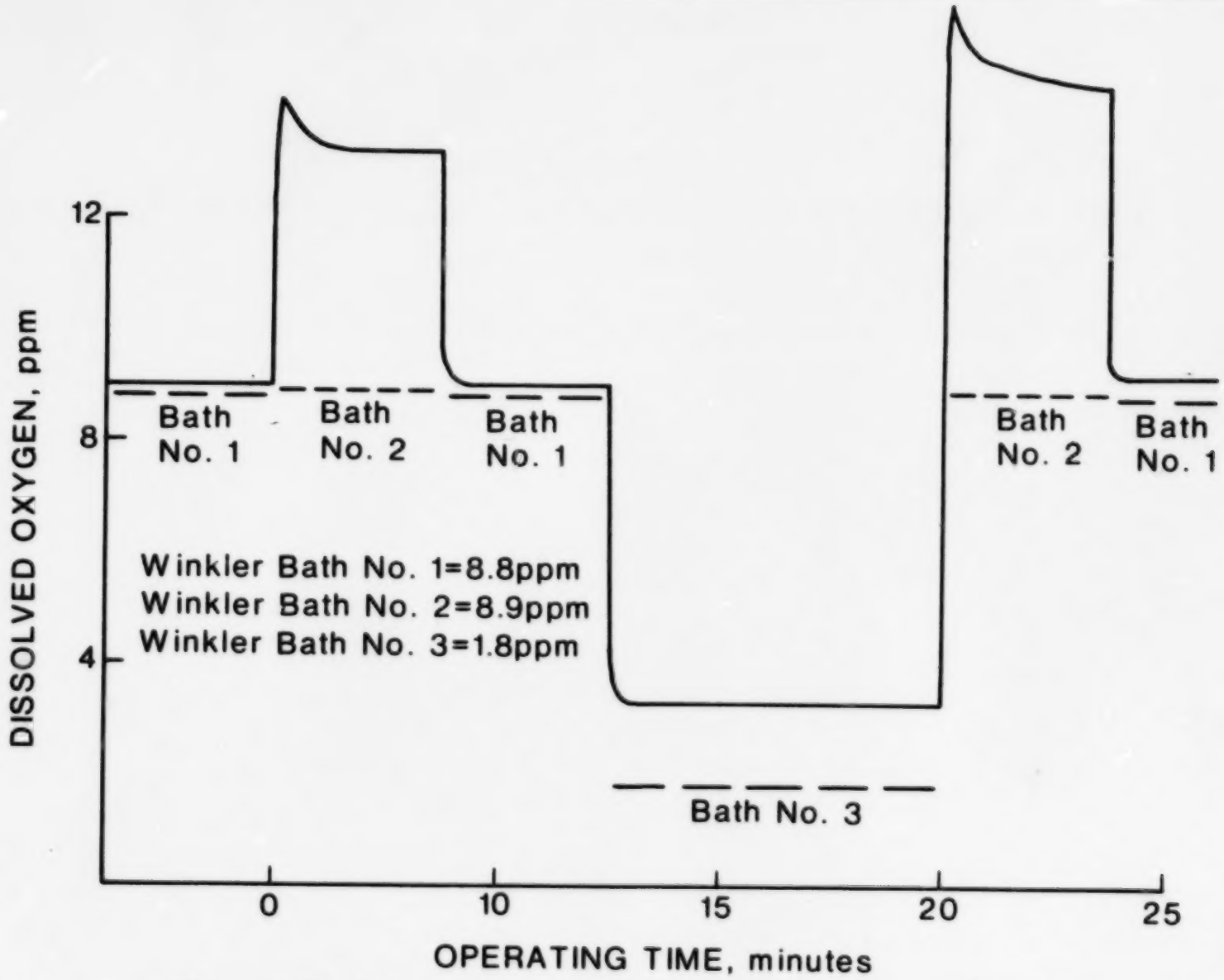

Figure 9. Ground Loop Problems in Transferring Sensor Between 20°C Baths

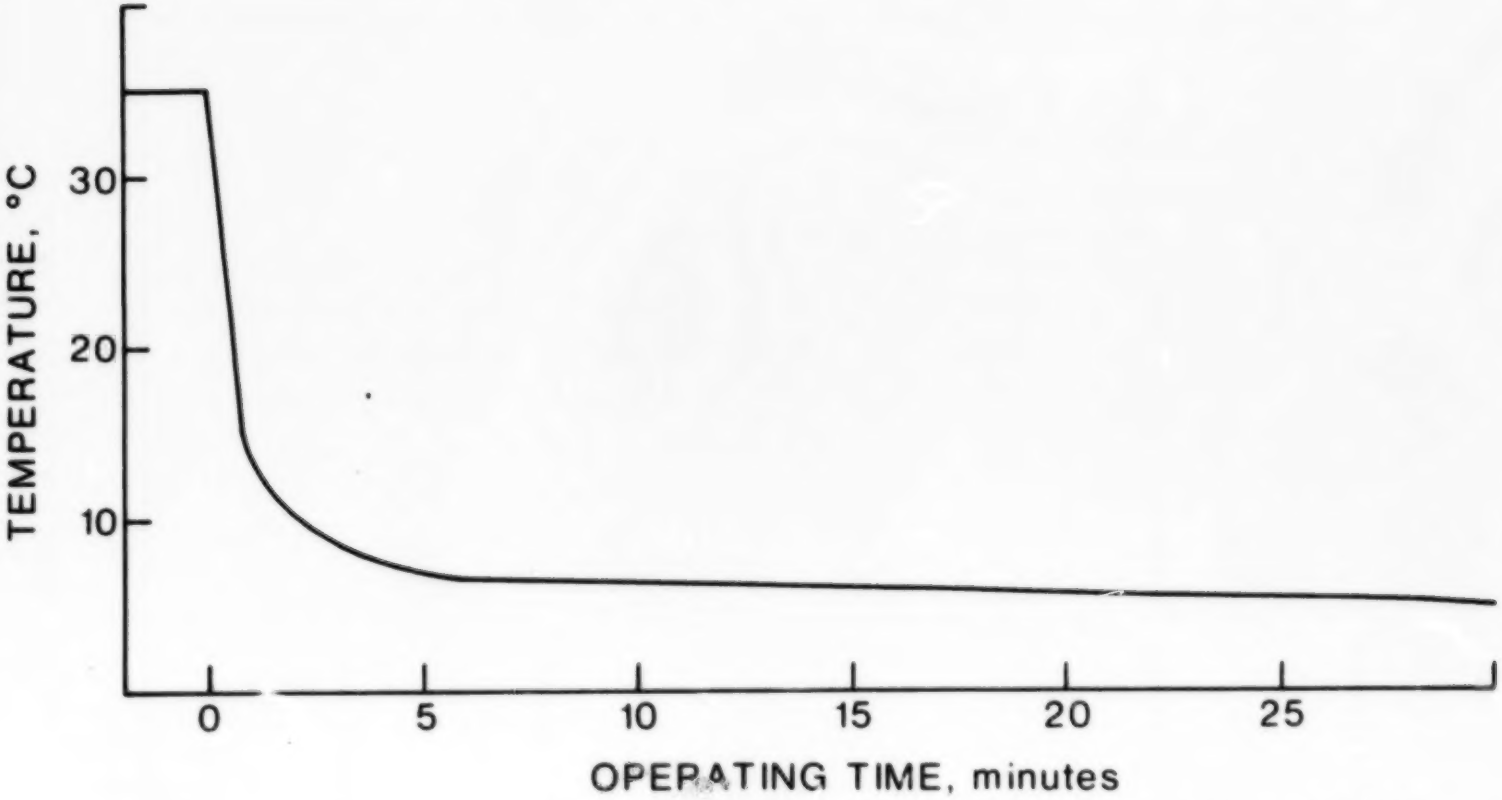

Figure 10. Transfer of Temperature Sensor from 35°C Bath to 5°C Bath

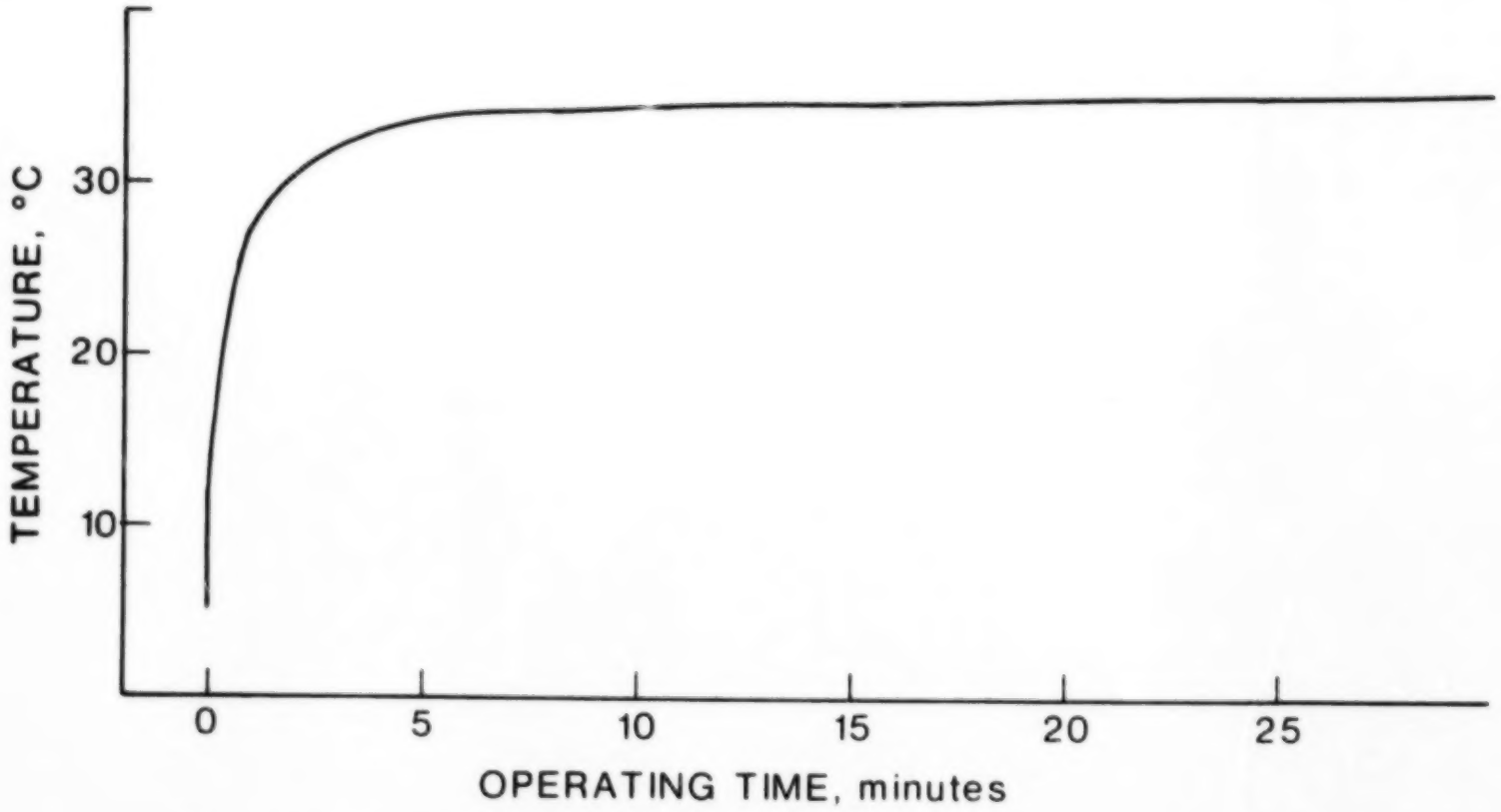

Figure 11. Transfer of Temperature Sensor from 5°C Bath to 35°C Bath